Computer simulation studies of HF adsorption on TiO$_2$ (001) and (110) surfaces

D M Tshwane[1,2*], R Modiba[1,2], H R Chauke[2], G Govender[1] and P E Ngoepe[2]

[1] Materials Science and Manufacturing, Advanced Materials and Engineering, CSIR, PO Box 395, Pretoria, 0001, South Africa

[2] Materials Modelling Centre, University of Limpopo, Private Bag X1106, Sovenga, South Africa

*DTshwane@csir.co.za

Abstract. Hydrogen fluoride molecule is a candidate used for etching metal oxide surface due to its strong corrosive qualities. However, the etching phenomenon is not well understood at the atomistic level. Investigation of HF interaction with TiO$_2$ (001) and (110) surfaces is important for enhancing the etching mechanism. Adsorption geometries and energies of HF on TiO$_2$ (001) and (110) surfaces have been investigated using density functional theory employing CASTEP code. It was found that HF chemically adsorbed to TiO$_2$ (001) and (110) surfaces to form Ti-F bond and hydroxyl molecule. The adsorption of HF molecule on TiO$_2$ (001) and (110) surfaces is by physisorption than chemisorption process. HF molecule prefers (001) surface with lower adsorption energy than on (110) surface. Besides, all these surfaces were found to have higher adsorption ability with increasing number of HF molecules. Mulliken charge analysis indicates that the dissociation of F atom attract electrons, due to the higher electronegativity of the fluorine atom.

1. Introduction

Titanium and its alloyed components are extensively used materials for a large variety of applications [1]. The adsorption of oxygen during the manufacturing of these metal components remain a big concern that results in the formation alpha case layer [2]. Surface modification is required due to the spontaneous growth of alpha case layer. Recently, wet chemical etching process remains a widely applied technique for surface modification using hydrogen fluoride (HF) as an etchant [3, 4]. HF is a colorless fuming liquid or gas molecule materials mainly used for industrial purpose such as metal surface etching. Metal surface etching by HF is one of the most important material tailoring technique in the manufacturing of metal-based alloyed components [5] therefore, it is very important to understand the interaction of HF with TiO$_2$ surfaces. Adsorption of HF by suitable solid adsorbents seems to offer an interesting and practical atomic interaction.

Considerable research effort has been expended for HF adsorption on the metal oxide surface [6, 7]. These studies, however, tend to have a focus on the Al$_2$O$_2$ [8], SiO$_2$ [9] surfaces and adsorption of a single prone molecule. Recently, Yang *et al* [10] showed that the adsorption of fluorine (F) ion on the surfaces of anatase-TiO$_2$ makes (100) surface energetically preferable than (101) surface. Wang *et al* [11] investigated selective etching phenomenon on (001) surface faceted anatase titanium dioxide. Their

results indicated that etching mechanism is energetically permitted and the surface etching can merely occur on the (100) surface under high HF concentrations. In this work density functional theory (DFT) approach is used to study the adsorption behavior of HF on TiO_2 (110) and (001) surfaces at different coverages. The adsorption energy, charge density difference and Mulliken charge are analyzed.

2. Computational methodology

First-principle calculations were performed using CASTEP code as implemented in Material Studio [12] on the basis of density functional theory (DFT). The electron-exchange and correlation were described by the Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) [13]. The GGA-PBE functional is well known to underestimate the band-gap which reduces photo-induced electron transfer during reactions [14]. To correct the strong electronic correlation problem, DFT+U method which was first initiated by Dudarev et al [15] was utilized with a U parameter of 5.0 eV for Ti in TiO_2 as proposed by Dompablo et al [16]. Brillouin-zone integrations are implemented using the Monkhorst-Pack approach [17] with K-point sampling grids of 4×4×1 for geometry calculation with cut-off energy of 400 eV. The TiO_2 (001) and (110) surfaces were represented by p(2×2) and p(3×3) supercell with five and seven atomic layers, respectively. In order to eliminate the interaction between two adjacent TiO_2, a vacuum of 30 Å was adopted. The interaction strength of HF molecule with the TiO_2 (001) and (110) surfaces is given by the adsorption energy, calculated using the equation below:

$$E_{ads} = [E_{HF/slab} - (E_{slab} + E_{HF})] \qquad (1)$$

where $E_{HF/slab}$ is the total energy of the surface slab with molecule, E_{slab} is the energy of the surface slab and E_{HF} is the energy of the isolated molecule.

3. Results and discussion

3.1 Surface geometry and HF Adsorption

Pure surface slabs were initially optimized to obtain surface energetic minima and examine chemical properties. Figure 1 (a-b) shows the optimized surface slabs with designated atom coordination, (a) TiO_2 (110) surface consisting of three coordinating oxygen atom (O3c) and both titanium five- and six-coordination atoms (Ti5c and Ti6c), respectively. (b) TiO_2 (001) surface consist of two coordinate oxygen atoms (O2c) and five coordinates titanium (Ti5c). Surface optimization reveal that TiO_2 (110) surface is much more stable with a lower surface energy of (1.98 Jm^{-2}) than TiO_2 (001) surface (2.81 Jm^{-2}).
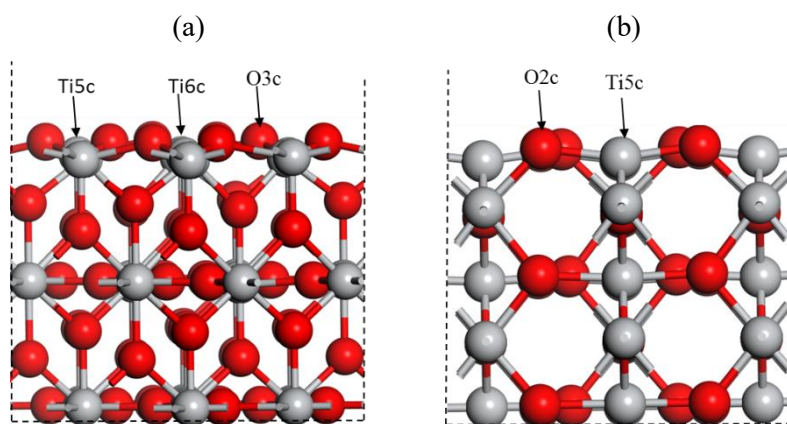

Figure 1: TiO_2 model surface slabs: (a) (110) and (b) (001) surface.

Calculated surface energies are well comparable with the results by Idrizz *et al* [18] and Tshwane *et al* [19]. The significant differences on the surface energy of TiO$_2$ (110) obtained by Tshwane *et al* [19], is due to different surface slabs. Adsorption process involves the interaction of HF molecule with TiO$_2$ (001) and (110) surfaces and one of the most fundamental characteristics of the process is the adsorption energy. Table 1 present the adsorption energies and the optimized parameters of HF molecule interacting with TiO$_2$ (110) and (001) surfaces. The negative value of adsorption energies indicates that the adsorption of HF molecule on Ti (001) and (110) surfaces is energetically favourable. TiO$_2$ (001) surface was found to be the most favourable adsorption surface than TiO$_2$ (110) surface with adsorption energy of -5.92 eV and -5.43 eV, respectively. The smaller E_{ads} value suggest very large exothermicity of the adsorption process. The relative difference in adsorption energy with a different surface is due to atom surface interaction and bonding.

Table 1: The optimized structure parameters and adsorption energies of HF on the TiO$_2$ (110) and (001) surfaces.

Surface slab	E$_{ads}$ physisorption	E$_{ads}$ chemisorption	Bond length Å		
			Ti-F	Ti-O	O-H
(001)-Ti5c	-5.92	-2.79	1.927	2.075	0.997
(110)-Ti5c	-5.43	-2.67	1.965	2.059	1.015
(110)-Ti6c	–4.93		1.984	2.086	1.022

Both physisorption and chemisorption were considered to investigate the nature of HF adsorption. The physisorption is the adsorption by bonding, whereas chemisorption is the adsorption without bonding. Comparing the adsorption energies, it was found that HF adsorption is by physisorption than chemisorption process. Figure 2 (a-b) present the optimized geometric structures of HF adsorption on Ti (110) and (001) surfaces. It was observed that HF dissociates completely when adsorbed on the TiO$_2$ (110) and (001) surfaces, with a hydrogen atom bonded to the oxygen atom forming hydroxyl while fluorine is bonded to five- and six-fold coordinated Ti atoms (Ti-F). The bond length of hydroxyl is about 0.99-1.022 Å and bond length of Ti-F is approximately 1.927-1.984 Å.
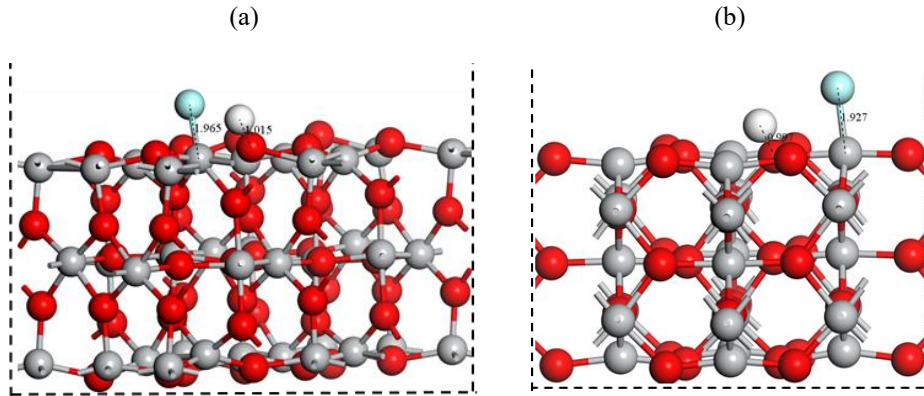
(a)   (b)

Figure 2: Optimized geometric structures of (a) HF-TiO$_2$ (110) and (b) HF-TiO$_2$ (001) surface.

The adsorption energies are shown to be the most thermodynamically favorable configuration. Figure 3 shows the dependence of adsorption energies per HF coverage on TiO$_2$ (110) and (001) surfaces. Results revealed that the adsorption energy become more stable with increasing HF coverage, this trend has been observed in several systems in the past [20]. However, the adsorption energies on (001) surface were found to be more stable than on (110) surface for all HF coverages. Therefore, attractive interaction between the HF molecules with the surface contribute to this phenomenon.
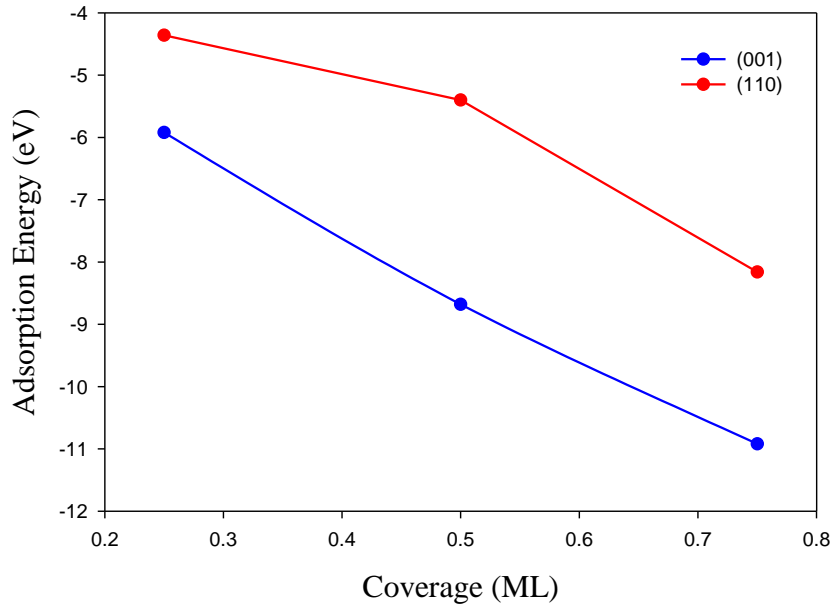

Figure 3: The adsorption energy of HF on TiO$_2$ (110) and (001) surfaces at different coverages.

3.2 *Charge density difference and Mulliken Charge analysis*

The interaction between the adsorbate and adsorbent implies a significant charge transfer. Charge density difference (CDD) between HF molecule with TiO$_2$ (001) and (110) surfaces were calculated using equation below:

$$\Delta\rho = \rho_{\frac{adsorbate}{slab}} - \rho_{slab} - \rho_{adsorbate} \tag{2}$$

where $\rho_{\frac{adsorbate}{slab}}$ is the charge density for the adsorbate system while ρ_{slab} and $\rho_{absorbate}$ are the charge densities for the non-interacting slab surface and adsorbate, respectively. Charge transfer influences the distribution of active species involved in the surface reaction, it becomes necessary to analyze the charge redistribution. The charge transfers between HF-TiO$_2$ (001) and (110) surfaces are visualized by plotting the 3D charge density difference as shown in figure 4. The blue and yellow iso-surface region represents the charge accumulation and depletion, respectively. A significant charge accumulation is established around the F atom forming electron rich region, whereas charge depletion is found around Ti atom.
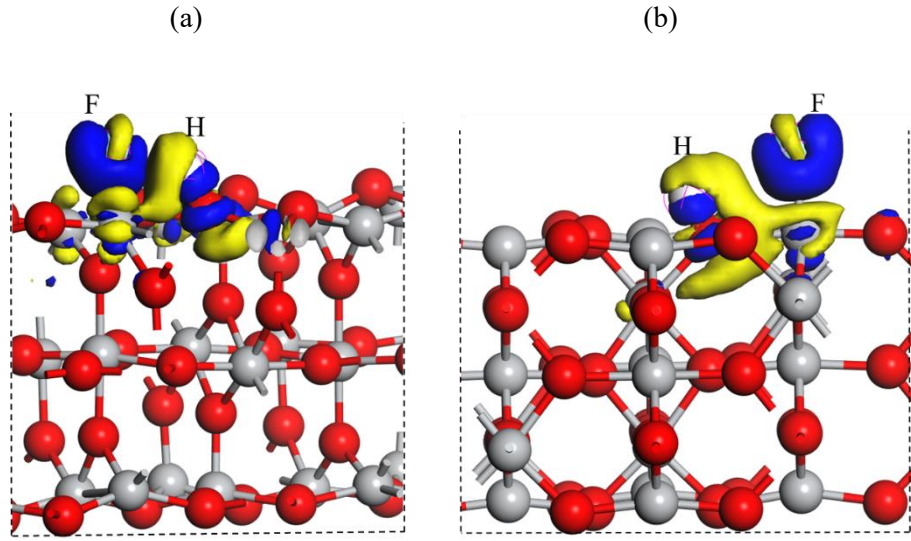
Figure 4: The charge density difference of HF adsorption on TiO_2 (a) (110) and (b) (001) surfaces with iso-surface value of 0.05 eV/Å^3.

Table 2 present Mulliken charge analysis for pure and adsorbed TiO_2 (110) and (001) surfaces. The Mulliken charge of Ti atoms in (001) and (110) surface are 1.34 e and 1.00 e, respectively. However, after adsorption Mulliken charge of Ti atoms increased to 1.47 e and 1.11 e for (001) and (110) surfaces, respectively. Comparing Mulliken charge analysis of clean surfaces and after adsorption, it is seen that electrons are transferred between HF molecule and TiO_2 (001) and (110) surfaces via F-Ti bonding. The electron transferred between F-Ti interaction for (001) surface is -0.13 e while for (110) surface is -0.11 e. This is due to the higher electronegativity of F atom than Ti atom.

Table 2: Mulliken charge analysis for Ti and F/Ti atoms.

surfaces	Mulliken Charge Analysis (|e|)		
	Ti	F/Ti	Δe^-
(001)	1.34	-0.49/1.47	-0.13
(110)	1.00	-0.51/1.11	-0.11

4. Conclusion

DFT calculations were employed to investigate the adsorption behaviour of HF molecule on TiO_2 (001) and (110) surfaces. It was found that HF molecule dissociates completely to form Ti-F and O-H bond. Adsorption behaviour of HF molecule is energetically favourable on TiO_2 (001) surface than on TiO_2 (110) surface. The adsorption energy value reveals that adsorption of HF molecule on TiO_2 (001) and (110) surfaces is by physisorption than chemisorption process, due to the stronger interaction between the F- ion and Ti atoms. The adsorption energy becomes more stable with increasing HF molecule coverage indicating that HF molecule coverage is thermodynamically stable. The interaction induced charge redistribution, according to charge density difference and Mulliken charge analysis it shows that HF-TiO_2 (001) and (110) surfaces have charge transferred process. Specifically, the electrons on the Ti atoms were transferred to HF molecule. This analysis showed patterns of electron accumulation and

depletion at the Ti-F interaction. Mulliken charge analysis indicated that titanium atom loses electrons whereas fluorine gains an additional electron during the interaction.

Acknowledgement

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